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DEPARTMENT OF CHEMISTRY
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CLEVELAND, OHIO 44106

TECHNICAL REPORT NO. 46

RECENT ADVANCES IN THE UNDERSTANDING OF ELECTROCATALYSIS AND ITS RELATION TO SURFACE CHEMISTRY

by

Ernest Yeager

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Ernest Yeager

Prepared for Presentation at the Symposium on
Electrode Materials and Processes for Energy Conversion
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Recent progress will be summarized in developing an understanding of the adsorption of hydrogen and various oxygen species on electrode surfaces and the role of these species in electrocatalysis. Major developments are occurring in the study of adsorbed species at gas-solid interfaces. The question is can electrochemists translate such gas-solid information to electrochemical interfaces and even make use of some of the elegent surface physics tools; in some instances, yes.

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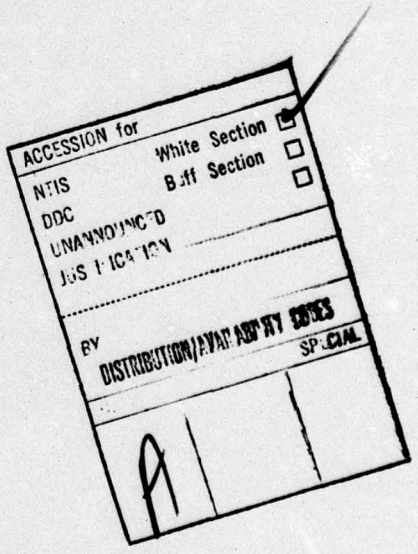

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RECENT ADVANCES IN THE UNDERSTANDING OF ELECTROCATALYSIS AND ITS RELATION TO SURFACE CHEMISTRY

by
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I. INTRODUCTION

Electrosorption plays a key role in electrocatalysis. Little information is available, however, concerning the chemical nature of the interactions of the adsorbed species with the electrode and even less about the adsorption sites. This situation has been detrimental to the development of electrocatalysis as a science. There is a general lack of good molecular level techniques for examining the chemical structure of electrochemical interfaces, analogous to the various spectroscopic techniques which have had such an impact on bulk phase chemistry. In most instances electrochemical techniques provide a sensitive tool for the detection of electrosorption but lack the needed molecular level specificity. Even the charge on electrosorbed species cannot be determined electrochemically because of the difficulty of resolving what fraction of the externally provided charge is transferred to the adsorbed species rather than just residing on the metal surface, compensating the charge of the electrosorbed species and the remainder of the ionic double layer (see e.g., ref. 1-5).

The most promising experimental approach for obtaining such molecular level information is in situ optical spectroscopy. Ultraviolet-visible reflectance spectroscopy, including ellipsometric spectroscopy, are sensitive to the surface electronic properties. Although a number of electrochemists have made use of these techniques to study electrosorption over the past decade, to date these measurements have provided little further understanding of the electronic features of adsorption. Much of the needed information is contained in the ultraviolet-visible reflectance and ellipsometric data but interpretation is a major problem -- not restricted to electrochemical interfaces.

Vibrational data for adsorbed species would also be very helpful. In situ infrared studies have been carried out (8,9) but have not yielded much information. Solvent absorption is a serious problem. In situ Raman (11,12) and particularly resonant Raman (13), where applicable, appear more promising for adsorbed organic species since solvents such as water are not a problem.

It is unfortunate that the elegant surface physics techniques such as LEED, UPS, XPS and Auger cannot be applied in situ to electrochemical studies. Even so, efforts are in progress to use these techniques in electrochemical studies with special procedures for minimiz-

ing structural changes during the transfer between the electrochemical and high vacuum environments.

The role of adsorbed species and surface layers in electrocatalysis will be reviewed for several electrode systems:

II. THE HYDROGEN ELECTRODE

In recent years, some general insights have been achieved into the relationship of hydrogen electrode kinetics to hydrogen adsorption. For a given mechanism the exchange current density is related to the standard free energy of adsorption of the particular type adsorbed hydrogen upon which the kinetics depend. This dependence is represented by the familiar volcano shaped curves (14-16), shown in Fig. 1, according to Parsons (14), for the following rate controlling steps:

I. Discharge: $H_3O^+ + e^- \rightarrow H_2O + H_{ad}$ (a)

II. Recombination: $2H_{ad} \rightarrow H_2$ (b)

III. Ion-plus atom: $H_3O^+ + H_{ad} + e^- \rightarrow H_2O + H_2$ (c)

where reaction I may be followed by either II or III. Reaction III may proceed with $(H\text{-}H)^+_{ad}$ as an intermediate; i.e.,

$$H_3O^+ + H_{ad} \rightarrow H_2O + (H\text{-}H)^+_{ad} \quad (c')$$

$$(H\text{-}H)^+_{ad} + e^- \rightarrow H_2 \quad (c'')$$

The flat portion of the curves corresponds to the Temkin region of the adsorption isotherm. In constructing the volcano curves the transfer coefficient relating the standard free energy of activation $(\Delta G^\circ)^=$ to the standard free energy change ΔG° has been taken to be 1/2; i.e., $\alpha = \Delta(\Delta G^\circ) = 0.5$. This may be open to question for Reactions II and III. Arguments can be put forth (17), based on Bond's model of non-activated adsorption of type C hydrogen (40), that $(\Delta G^\circ)^\ddagger$ approaches ΔG° for Reaction II on some metals. Further it is likely that the activated state for this reaction involves the direct interaction of both hydrogens with the surface rather than an end on interaction of a H-H intermediate. Consequently, the transfer coefficient α for Reaction III may also approach unity rather than 1/2. Under such circumstances, the volcano curves take on the form (17) indicated in Fig. 2, using a combination of Breiter's data (18) and Ludwig's data (17) (extended to 3M HCl) as a few calibration points.

The experimentally observed behavior of hydrogen overpotential on various metals correlates reasonably well with Fig. 2. Metals such as Hg, Tl, Zn, Cd and Pb which adsorb hydrogen weakly (positive values of ΔG°) have low values for the apparent exchange current density, Tafel

slopes of -2RT/F and Reaction I as rate controlling. Metals such as Pt and the Pt family with ΔG° values close to 0 have high apparent exchange current densities and kinetics which indicate that Reaction II follows Reaction I and is rate controlling. Metals such as Mo, Ta and W which strongly adsorb hydrogen again have low exchange current densities and kinetics which indicate Reaction III follows Reaction I and is rate controlling.

An important implication of the volcano curves is that it is unlikely a catalyst will be found with an exchange current density higher than that for Pt since this metal has ΔG° close to 0. The main thrust of applied research on hydrogen electrocatalysts should be the finding of catalysts with higher exchange currents per unit cost and resistance to poisoning and to loss of area when used in high area forms.

Various authors have examined the discharge step I theoretically, taking into account the possibility of proton tunnelling (for a review, see ref. 20). Bockris and Matthews (21) have proposed the model in Fig. 3. The vertical transition ΔE_o corresponds to the transfer of an electron from the Fermi level of the metal to the H_3O^+ ion with no change in the reaction coordinate. Radiationless electron transfer (tunnelling) occurs at the intersection of the two Morse curves from the metal to the vibrationally excited H_3O^+. The various electron energy levels in the metal correspond to translation vertically of the Morse curve for the initial state. The principal levels contributing to the discharge current are those within kT of the Fermi level.

Several electrochemists have considered proton tunnelling through the barrier rather than over the barrier. Bockris et al. (21,22) using a symmetrical Eckart barrier have concluded that proton tunnelling is important to hydrogen discharge on Hg and compatible with linear Tafel behavior. Christov (23-25) reached a similar conclusion using symmetrical and asymmetrical Eckhart and parabolic barriers. Conway (26) treated proton tunnelling, assuming the proton to originate from a water molecule immediately adjacent to the surface with a very thin barrier (0.5Å). This model results in high tunnelling probability but high Tafel slopes at low overpotentials and non-linear Tafel behavior at higher overpotentials ($-\eta > 0.5V$), which is contrary to the experimental data for Hg. Conway and Salomon (27) have concluded that proton tunnelling is not important for proton discharge even at temperatures down to -110°C in methanol. (The activation energy is essentially independent of temperature.)

Levich (28) has questioned the validity of using the Gamow tunnelling equation for proton discharge because of complications associated with solvent polarization fluctuations. Bockris and Sen (31) have rebutted this argument by attempting to show that the proton tunnelling occurs in a time considerably less than the 10^{-13}s and hence short compared to the solvent relaxation times.

The Bockris-Matthews model in Fig. 3 does not take into account resonance interactions at the intersection of the Morse curves. Salomon, Enke and Conway (30) and Bockris and Sen (31) have applied the semi-empirical bond-energy bond order method (BEBO) to calculate the potential energy surface. Bockris and Sen arrive at a value of 15 kcal/mole for the height of the barrier for Hg, which seems reasonable.

Dogonadze, Kuznetsov and Levich (32,33) have treated Reaction I using a quantum statistical mechanical approach which is an extension of their earlier outer sphere electron treatment. The proton as well as electron transfer are assumed to be fast subsystems with the solvent a slow system. Their treatment is interesting but unfortunately does not include the contribution to activation associated with stretching of the $H\text{-}OH_2$ and H-M bonds. The recent quantum statistical mechanical treatment of Kharkats and Ulstrup (34) takes into account not only the bulk solvent polarization contributions but also discrete modes around the reaction centers which they considered to be a solvated $H_9O_4^+$ ion. These authors show that anharmonicity can account for the extended Tafel linearity observed over more than 1V on metals such as Hg.

Hydrogen electrode kinetics are of special interest on Pt because of its high catalytic activity. Various workers (35-37) have found a Tafel slope for the cathodic branch of -RT/2F and high exchange current densities (e.g., $\geq 10^{-2} A/cm^2$). Two explanations have been advanced for this behavior. Schuldiner (35) and Bockris et al. (36) have used a mechanism involving Reactions I and II (discharge followed by atomic recombination) with Reaction II rate controlling. Breiter (38) has proposed pure diffusion control involving dissolved H_2. On the basis of ultrasonic (36) and rotating disk-ring (39,19) measurements, Yeager et al. have proposed that the cathodic process is controlled by combined H_2 diffusion and recombination kinetics. Parsons (14) and Krishtalik (41) have offered theoretical arguments for desorption by Reaction II as rate controlling.

The anodic oxidation of H_2 exhibits first order dependence on H_2 concentration (42) and most workers consider the dissociative adsorption of H_2 (the reverse of Reaction II) as rate controlling (see e.g., 42-45). Here again, however, the high exchange current density makes it difficult to examine the kinetics without transport of dissolved H_2 to the electrode surface being the predominant control, even with the rotating disk electrode technique (19,42,46), particularly with Pt electrodes which have relatively high area and hence high activity as a result of repeated cycling to anodic potentials prior to the H_2 oxidation measurements.

A problem associated with H_2 formation with the kinetics controlled by Reaction II is that the -RT/2F slope is to be expected with low H(ads) coverage (35). On the other hand, various electrochemical measurements including impedance (e.g. 47), linear sweep voltammetry

(see e.g., 48-51) and charging curves (e.g., 52,53) indicate that total H(ad) coverage is already close to unity at the reversible potential. This problem can be resolved by assuming that two types of H(ads) are involved in the overall electrode process and that the adsorbed hydrogen involved in Reaction II is at low coverage, as suggested by Schuldiner (35,43). The existence of several types of adsorbed hydrogen on Pt appears fairly evident from the various electrochemical measurements of adsorbed hydrogen just cited. Thus the H_2 formation may be represented as follows:

$$H_3O^+ + e^- \rightarrow H_A \qquad (d)$$

$$H_A \rightarrow H_B \rightarrow \text{---} H_j \qquad (e)$$

$$H_i + H_j \rightarrow H_2 \qquad (f)$$

where H_i and H_j may or may not be the same; steps d and e are essentially reversible; and one or more of the forms of H(ad) are at high coverage but the sites available for H_i and H_j type adsorption are at low coverage. Considering combined kinetic and diffusion control with Langmuir behavior for H_i and H_j, the current-potential behavior for the anodic as well as cathodic branches is described by the equation

$$\ln[i/(1-\exp\tfrac{2F\eta}{RT})] = -\frac{2F\eta}{RT} + \ln X_o \qquad (1)$$

where

$$\frac{1}{X_o} = \frac{1}{i_o} + \frac{1}{i_d} \qquad (2)$$

i_j is the anodic diffusion limiting current density for H_2 transport, i_o^j is the exchange current density for Reaction j, η is the overpotential and the other symbols have their usual meaning. This equation has been tested for Pt by Ludwig et al. (17,19) using the rotating disk technique and fits the data quite well (see Fig. 4). The values of i_o evaluated for Pt in 6.1M HCl for a H_2 pressure of 1 atm at 25°C are $i_o = 8 \times 10^{-3} A/cm^2$ for Pt not roughened by cycling to anodic potentials.

The question remains open as to what type of adsorbed hydrogen is involved in the desorption reaction f. It is unlikely that H_i and H_j correspond to any of the hydrogen peaks observed by linear sweep voltammetry and other electrochemical techniques on Pt. Nonetheless, it will be helpful to understand the various factors contributing to up to five hydrogen peaks observed in the voltammetry curves. Various explanations have been proposed including different adsorption sites on a given single crystal surface, a distribution of crystallographic surfaces, induced heterogeneity associated with hydrogen adsorption itself (50) and anion adsorption which induces heterogeneity by blocking sites to varying degrees and perturbing adjacent sites (51). The

pronounced dependence of the hydrogen electrosorption on the type and concentration of anion (Fig. 5) indicates that hydrogen adsorption-desorption are coupled to anion desorption-adsorption (51).

In an attempt to resolve this problem, various electrochemists have examined hydrogen electrosorption on single crystal Pt. Will (54) examined the low index planes (100), (110) and (111) and found the same two major peaks on these three orientations although the relative heights depended on the crystal orientation. The single crystal Pt electrodes studied by Will probably did not expose a single crystallographic surface. The distribution of cystallographic surface planes depends on the overall orientation and the extent to which the surface has been cycled to anodic potentials. Will arrived at the conclusion that the strongly adsorbed hydrogen peak IV (Fig. 5) corresponds to the 100 plane and the weakly adsorbed peak I to the (110) plane. Rather analogous results have been reported by Bronel et al. (56) for the (100) and (111) Pt surfaces. These workers used electron microscopy to establish that the surfaces were facet-free. Kinoshita and Stonehart (57) have examined hydrogen adsorption on dispersed Pt as a function of crystallite size and find a dependence which they interpret as further evidence that the multiple peaks result from different surface crystallographic structures.

In contrast, Bagotzky et al. (55) and Conway et al. (50) have concluded from their single crystal Pt studies that there is little difference in the hydrogen adsorption on the (100) (110) and (111) planes. Conway et al. (50) attribute the multiple peaks principally to induced heterogeneity arising from collective long range electronic interactions.

The probability is high in all of the single crystal studies just cited that the surface prevailing during the electrochemical measurements does not correspond to a single crystal plane. Even if the Pt crystal has only one plane predominant before the electrosorption measurements, these authors generally cycled their electrodes to anodic potentials in the anodic film region to oxidize or desorb interferring surface contaminants and this procedure is likely to cause restructuring.

Recently several groups have attempted to devise techniques which permit the introduction of a single crystal surface of predominantly one plane and free of impurities into an electrochemical environment with a minimum possibility of restructuring and contamination. These include A. Hubbard at the University of California at Santa Barbara (58,59), J. A. Joebstl at Fort Belvoir (60), Ross at United Technology (60) and the author's group at Case Western Reserve University (61). Each group has turned its attention to the (100), (110) and (111) planes of Pt and first establishes that the surface is predominantly one plane using low energy electron diffraction (LEED) and free of surface impurities down to a few percent of a monolayer using Auger

electron spectroscopy.

The results obtained by Ross (62) and in the author's laboratory by O'Grady et al. (63) will be presented in separate papers in this symposium. The key features of the techniques used by O'Grady et al. are vacuum transfer; thin-layer electrochemical cell techniques to avoid contamination; and introduction of the Pt single crystal surfaces into the electrolyte at controlled potentials in the hydrogen adsorption region. In the cyclic voltammetry studies of hydrogen electrosorption, the potential range is restricted to +0.05 to 0.40V vs. RHE to reduce any possible restructuring. The voltammetry curves on the single crystal Pt surfaces retract with repeated cycling, starting with the very first sweep. If the voltage sweep is extended into the anodic film formation region to $\geq$1.4V vs. RHE, the hydrogen adsorption region changes significantly with new peaks appearing or very minor peaks becoming major peaks, depending on the original surface. This is probably the result of restructuring although the possibility exists that oxygen has been irreversibly adsorbed into sites within the surface layer.

On the (100) Pt surface, Hubbard et al. (59), Ross (62) and our group (63) find one predominant peak (Fig. 6) corresponding to the strongly adsorbed hydrogen peak on polycrystalline Pt in acid solutions. The LEED pattern for the Pt (100) indicates a 5 x 20 overlayer mesh (58,64). This surface probably reverts to (1x1) in contract with the electrolyte. On the (111) surface, our group finds only a minor peak corresponding to weakly adsorbed hydrogen while Ross and Hubbard et al. report a major peak. The source of this discrepancy is not fully clear but may be caused by the cycling of the electrode to anodic potentials in the case of Ross' work and possibly also Hubbard et al. Alternatively our (111) Pt surface may have some of the sites blocked by an impurity but on the other hand Auger does not indicate any such impurity. In any event, the presence of only one major peak on the (100) Pt surface provides strong evidence that the principal peaks on polycrystalline Pt correspond to different crystallographic planes.

A number of theorists are presently involved in calculating the relative bond energies for hydrogen and other species on various sites on metal surfaces, using extended Hückel molecular orbital theory, LCAO, and Xα scattering. These types of calculation can contribute substantially to the understanding of electrochemical interfaces. Leban and Hubbard (65) have used extended Hückel molecular orbital theory to predict the most stable sites for various species including H_2O, OH^-, H, the halides and Pt on (111) Pt. The most stable sites for these species are shown in Fig. 7. According to their calculations, the preferred sites for hydrogen adsorption on the (111) surface are in the plane between three adjacent Pt. While substantial questions exist as to the validity of various assumptions in such calculations, nonetheless, they present an important step in the development of a theoretical basis for electrocatalysis. [For a review, see (126,127.)]

III. THE OXYGEN ELECTRODE

The oxygen electrode reactions are less well understood than for the hydrogen electrode. The pronounced irreversibility of the oxygen electrode reactions at moderate temperatures has severely complicated mechanistic studies. The exchange current densities for the oxgyen electrode are very low -- typically 10^{-10} to 10^{-11} A/cm^2 on an effective catalytic surface such as platinum at room temperature. Consequently the current densities near the reversible potential are generally too low to permit measurements under conditions where the kinetics are sensitive to the reverse as well as forward reactions. Further, the experimentally accessible portions of the cathodic and anodic branches of the polarization curves are sufficiently separated in potential that the surface conditions differ very substantially. Therefore, the cathodic and anodic processes under these conditions are probably not the reverse of each other. To complicate the situation further, the oxygen electrode reactions may proceed through a large number of pathways. This explains why the mechanisms of O_2 generation and reduction are still not fully understood even on platinum, the most extensively used and most studied O_2 electro-reduction catalyst.

Before discussing O_2 electrocatalysis on specific non-metallic surfaces, some of the general features of the possible electrode mechanisms will be considered. O_2 reduction in aqueous solutions requires a strong interaction of O_2 with the elctrode surface for the reaction to proceed at a reasonable rate. Three types of models for such interaction have been proposed (66,67). These and the corresponding likely reaction pathways for O_2 reduction are those in Fig. 8. The Griffiths model involves a lateral interaction of the π-orbitals of the O_2 interacting with empty d_{z^2} orbitals of a transition element, ion or metal atom with back bonding from at least partially filled d_{xz} or d_{yz} orbitals of the transition element to the π^* orbitals of the O_2. This type of interaction should lead to a weakening of the O-O bond with a corresponding lengthening of this bond. The Vaska complexes [e.g., $Ir(O_2)Cl(CO)(PPh_3)_2$] appear to form such complexes with O_2 (71,72). These compounds are selective oxidation catalysts for cyclic olefins (73). The formation of a strong metal-to-oxygen interaction results in a weakening of the O-O bond and an increment in the length of this bond (74). Sufficiently strong interaction of this type may lead to the dissociative adsorption of O_2 with probably simultaneous proton addition and valency change of the transition element in the manner represented by Pathway I in Fig. 1, followed by reduction of the $M(OH)_2$ to regenerate the catalyst site. Sandstede et al. (75,76) have attempted to explain oxygen reduction with square pyramidal Co(II), Fe(II) and Fe(III) complexes as well as on the thiospinels on the basis of such π bonding. Tseung, Hibbs and Tantram (77) have proposed that O_2 reduction on Li-doped NiO changes from a non-dissociative to dissociative mechanism above the Neel point (200°C for their ~10-atom % Li-doped NiO) in order to explain the increment in catalytic activity in KOH hydrate melts above the Neel temperature.

With most transition metal catalysts, the most probable structure for O_2 adsorption is the Pauling model (69) in which sp^2 orbitals of O_2 interact with d_z^2 orbitals of the transition metal. The square pyramidal complexes of Fe(II) and Co(II), which have good activity for O_2 reducation in acid solutions, appear to involve such an end-on interaction on the basis of esr and other evidence (78). This adsorption of O_2 is expected to be accompanied by at least a partial charge transfer to yield a superoxide and then peroxide state, as represented by Pathway II in Fig. 7. The adsorption of the O_2 on the square pyramidal complexes of Fe(II) and Co(II) may lead directly to the superoxide state. With somewhat similar oxyhemoglobin complexes of iron, various workers have proposed that O_2 binding to the iron involves O_2^- or $O_2^=$ states with Fe in the III valent state (79-81). The change in valency state of the transition metal coupled with the change in O_2 oxidation state during formation of the O_2 adduct corresponds in principal to the redox electrocatalyst concept proposed by Beck et al. (82,83).

The further reduction of the O_2 beyond the peroxide state requires rupture of the O-O bond. Such can occur in Pathway IIB through the formation of O^- or $HO\cdot$ free radicals in solution or the simultaneous reduction-bond cleavage (electrochemical desorption) to yield H_2O or OH^-. Neither of these processes are likely to be sufficiently fast at practical operating potentials for O_2 cathodes but the electrochemical desorption is a better candidate. The free energies of formation of the O^- and $HO\cdot$ free radicals in solution are just too high to achieve sufficiently high concentrations for the subsequent homogeneous reactions to proceed at rates corresponding to reasonable current densities at acceptable electrode potentials. Substantial evidence exists for Pathway IIA yielding solution phase peroxide for various metallic and non-metallic electrode surfaces. With non-metallic electrodes such as carbon, graphite and lithiated NiO in aqueous alkaline solutions, significant amounts of peroxide are found in solution and the potential under open-circuit conditions follows the Nernst equation predictions for the O_2-HO_2^- couple (see e.g., ref. 84,85) providing the surfaces are free of traces of Pt and other contaminants which catalyze peroxide decomposition or reduction.

Under some circumstances it is possible that the superoxide species $O_2^{-\cdot}$ may desorb to yield the solution phase species. This ion is formed as a reasonably stable entity during O_2 reduction in aprotic solvents (see e.g., ref. 86-89) and probably in carbonate melts (90). The superoxide ion also has been proposed to be formed in aqueous solutions on Hg (91,92), amalgamated gold (93) and carbon paste (94) cathodes in the presence of surface active agents. Under these circumstances, Divisek and Kastening (91,92) propose that the surfactant molecules displace water molecules from the surface, impeding access of water to the adsorbed $O_2^{-\cdot}$, and thereby inhibiting further reduction. Dubrovina and Nekrasov (93) have proposed that the $O_2^{-\cdot}$ radical may be stabilized through the formation of a complex with the surfactant molecule. In the absence of adsorbed organic species, however, it does not appear in alkaline solutions that an $O_2^{-\cdot}$ desorption mechanism contributes significantly to the observed current. Rotating disk

experiments have rather clearly demonstrated this for graphite and also gold cathodes (96,97).

Pathway III in Fig. 8 provides an alternate means for bringing about rupture of the O-O bond through the formation of an -O-O-bridge. Such a mechanism may come into play with the proper surface spacing of transition metal atoms or ions in a metal, oxide or thiospinel or in a bimetal complex such as a macrocycle. The formation of the bridge species also requires that the two metal species have partially filled d_{xz} or d_{yz} orbitals to participate in bonding with the sp^2 orbitals of the oxygen. Macrocyclic transition metal complexes of the type $M-O_2-M$ have been synthesized (e.g., see ref. 98-101) and appear to occur naturally in hemeythrin.

For any of the mechanisms in Fig. 8, considerable questions exist as to the reversibility of the O_2 adsorption step at the rather high rates involved with practical O_2 cathodes. For O_2 to bond to M^z will generally require the replacement of a water molecule or anion of the electrolyte -- a situation which would normally be expected to be unfavorable to O_2 unless the O_2 adduct has a pronounced dipolar character $(M^{z+1}O\text{-}O^-)$ (102,103).

At steady state any peroxide formed on the electrode surface must be subsequently further reduced or decomposed. When the O_2 reduction proceeds entirely through a peroxide state on the electrode surface and/or in the solution, the process is usually referred to as "series" whereas when O_2 reduction proceeds simultaneously by a dissociation step without a peroxide state as well as through a peroxide state, the processes are described as "parallel". Peroxide has been detected in the solution phase during O_2 reduction on many metallic and non-metallic electrodes (e.g., Pt, Au, Ag, Pb, Ni, NiO, carbon, graphite) in various aqueous electrolytes at $T < 100°C$. Consequently little doubt exists that the peroxide mechanim is often functional.

Various workers have used the rotating disk-ring electrode to examine the kinetics of O2 reduction on a number of metal and non-metal surfaces and particularly to establish whether the series or parallel schemes are applicable. Damjanovic, Genshaw and Bockris (104) proposed that a potential dependent intercept for the plot of i/i_R vs. $1/\sqrt{\omega}$ plot constituted evidence for the parallel mechanism (i=disk current, i_R=ring current, ω=angular rotation rate). The kinetic analysis by Damjanovic et al., however, did not consider a potential dependent electrodesorption of peroxide. When such is included in the analysis, it is found that the series mechanism can also yield a potential dependent intercept (105-107). Wroblowa et al. (106) has called attention to the fact that the correlation of the intercept of the i/i_R vs. $1/\sqrt{\omega}$ plot with the slopes at various potentials can serve as a diagnostic test for the parallel mechanism.

Electrode surfaces on which O_2 reduction proceeds predominantly by the series mechanism through a peroxide intermediate include gold (97, 105,113), graphite and various carbons (84,109-111) including glassy carbon (112). The parallel mechanism appears operative on Pt (108, 114,117), Ir (124), Rh (114), Pt-Rh alloys (116) and Pd (114,115).

Much more complete kinetic data are available for the two-electron O_2 reduction to peroxide on a surface such as gold than for the overall four electron reduction to water or OH^- on a surface such as Pt. The rotating disk-ring studies of Zurilla et al. (97,105) in alkaline solutions have yielded a stoichiometric number (2.0) and Tafel slopes and reaction orders for the forward and reverse reactions which support the following mechanism (97,105):

$$O_2 + e^- \rightarrow O_2^- \text{ (ads)} \qquad \text{(g)}$$

$$2O_2^- \text{(ads)} + H_2O \rightarrow HO_2^- + O_2 + OH^- \qquad \text{(h)}$$

with reaction g rate controlling and reaction h fast. Reaction h may be multistep. These reactions involve adsorbed O_2^- and not the corresponding solution phase for radicals. Evidence for such can be deduced as follows (97): if a solution phase dismutation reaction equivalent to reaction h were involved, then it must occur within the Nernst boundary layer; otherwise the rotating disk experiments could not indicate two electrons per O_2 reaching the electrode surface. On the other hand, an upper limit can be set for the O_2^- concentration in the solution adjacent to the electrode on the basis of the reversible potential for the O_2/O_2^- couple. Further an upper limit for the second-order solution phase dismutation reaction is known from radiation chemistry studies. This permits an upper limit to be set for the current density compatible with reaction h as a solution phase process. The values so calculated are typically three orders of magnitude below the experimental values (97,118). Thus reaction h must be a heterogeneous one.

The further reduction of HO_2^- to OH^- is first order in HO_2^- and the rate constant has very little potential dependence. This suggests a chemical step preceding the electron transfer as rate controlling; e.g.

$$HO_2^- + H_2O \rightarrow 2OH\text{(ads)} + OH^- \qquad \text{(i)}$$

In both acid and alkaline solutions hydrogen peroxide is generated during O_2 reduction on Pt. The O_2 reduction to H_2O or OH^- by a parallel pathway not involving H_2O_2 or HO_2^- is predominant on reduced Pt in the absence of adsorbed impurities (108,114,117). A Tafel slope of -RT/F is observed in the region corresponding to the start of anodic film formation where Conway et al. (50) and others (119) assign the structure in the linear voltammetry curves to essentially reversible OH adsorption; i.e., 0.8 to 0.95V vs. RHE. At more cathodic potentials the slope shifts to -2RT/F or a transfer coefficient of 1/2. Similar

behavior has been observed in ~85% H_3PO_4 (108,120-122). Damjanovic et al. (117) have explained this behavior on the basis of the dissociative adsorption of O_2. Specifically Damjanovic et al. (117,124) proposed two possible pathways, expressed for alkaline solutions as follows:

<u>Mechanism I</u>:

$$M + O_2 \rightarrow 2M\text{-}O \quad (j)$$

$$2[M\text{-}O + e^- \rightarrow M\text{-}O^-] \quad (k)$$

$$2[M\text{-}O^- + H_2O \rightarrow MOH + OH^-] \quad (l)$$

$$2[MOH + e^- \rightarrow M + OH^-] \quad (m)$$

Mechanism II:

$$M + O_2 \rightarrow 2M\text{-}O \quad (n)$$

$$2[M\text{-}O + H_2O \rightarrow M\text{-}O\text{-}H\text{-}OH\ ] \quad (o)$$

$$2[M\text{-}O\text{-}H\text{-}OH + e^- \rightarrow M\text{-}O\text{-}H\text{-}OH^-] \quad (p)$$

$$2[M\text{-}O\text{-}H\text{-}OH^- \rightarrow M\text{-}OH + OH^-] \quad (q)$$

$$2[M\text{-}OH + e^- \rightarrow M + OH^-] \quad (r)$$

Mechanism I is similar to that proposed by Krasilshchikov (123) in 1963. With Mechanism I, Damjanovic et al. propose reaction l as rate controlling at low cathodic overpotentials and k rate controlling at high cathodic overpotentials, thus accounting for the shift in slopes. With Mechanism II, reaction q is rate controlling at low cathodic overpotentials and reaction p at high overpotentials.

Tarasevich (114) has proposed a different pathway for O_2 reduction to water that involves adsorption of O_2 without charge transfer; i.e.,

<u>Mechanism III</u>:

$$M + O_2 \rightarrow M\text{-}O_2 \quad (s)$$

$$M\text{-}O_2 + e^- + M + H_2O \rightarrow MO + MOH + OH^- \quad (t)$$

with the peroxide reaction coupled as follows:

$$M\text{-}O_2 + e^- \rightarrow M\text{-}O_2^- \quad (u)$$

$$M\text{-}O_2^- + e^- + M + H_2O \rightarrow M + HO_2^- + M\text{-}OH^- \quad (v)$$

Tarasevich (114) assumes that the slow steps for both the overall $4e^-$ reduction and the peroxide mechanism are the first electron transfer relations t and v. Tarasevich then considers the effects of surface coverage of M-O and M-OH on the kinetics of these steps assuming that $M\text{-}O_2$ coverage is low and assuming Temkin type behavior with respect to M-O and M-OH. The transition from the low to higher Tafel slope results as M-O coverage becomes significant. The potential region which Tarasevich assigns to M-O formation on Pt, however, is attributed by

Conway et al. (50) and our group (119) to reversible adsorption of MOH^-. The basic concept that the shift in Tafel slope is associated with the reduction of the anodic film, however, appears correct, as has also been proposed by Damjanovic and Genshaw (125).

Time restrictions prevent a discussion of O_2 electrooxidation catalysis.

In summary, the science of electrocatalysis is still in the infancy but there are promising signs on the horizon for more rapid growth, the most significant of which is that theorists, surface physicists and inorganic chemists joining forces with electrochemists to attack this area as part of the overall field of heterogeneous catalysis.

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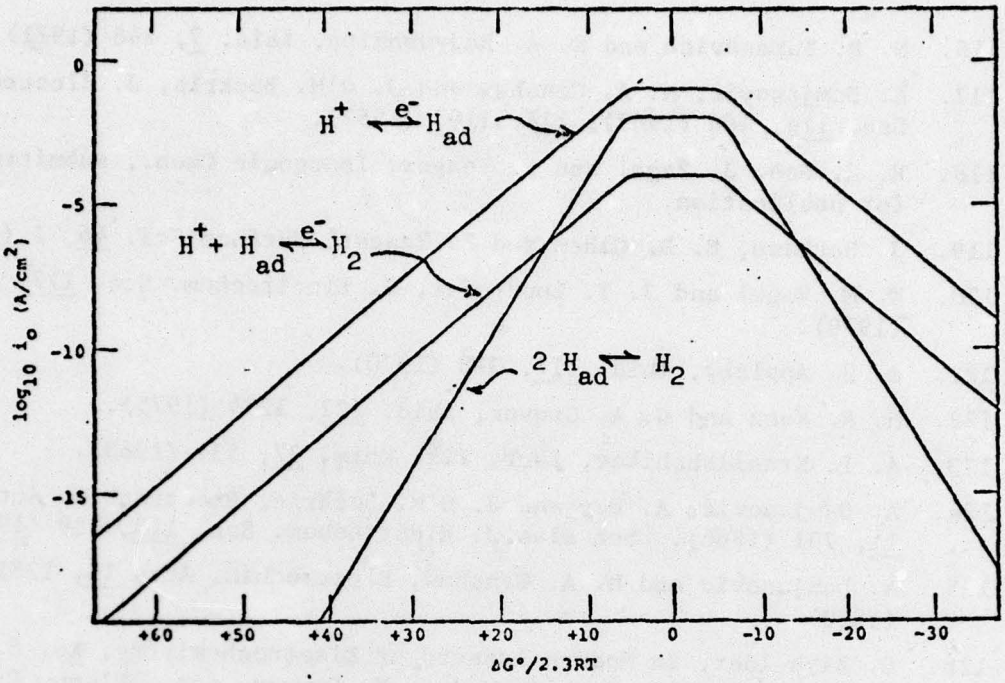

Fig. 1. Exchange currents at the hydrogen electrode and the standard free energy of adsorption of hydrogen.

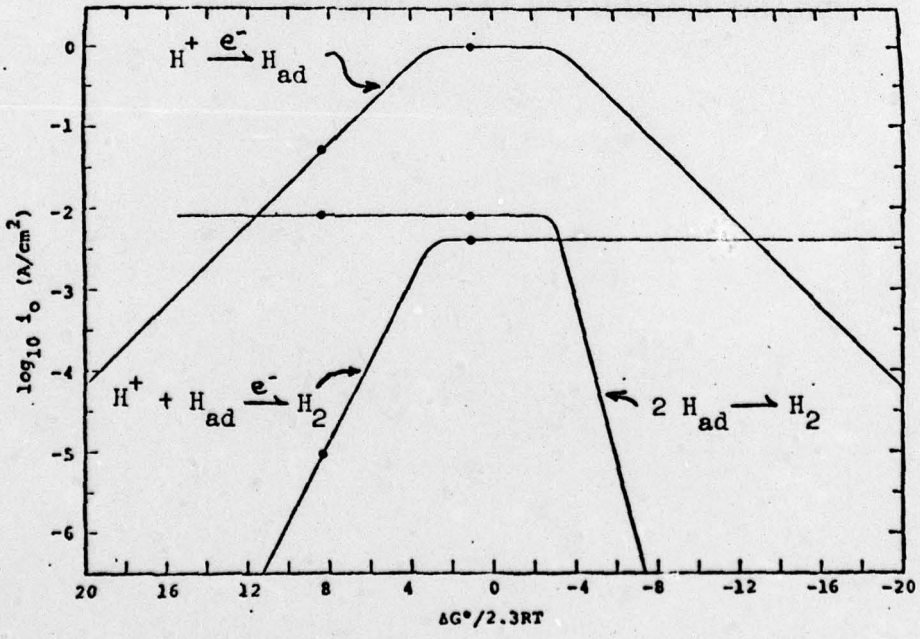

Fig. 2. Volcano curves in 3M HCl with $_{I}$ = 0.5; $_{II}$ = 1; $_{III}$ = 1. [Ludwig and Yeager(17)].

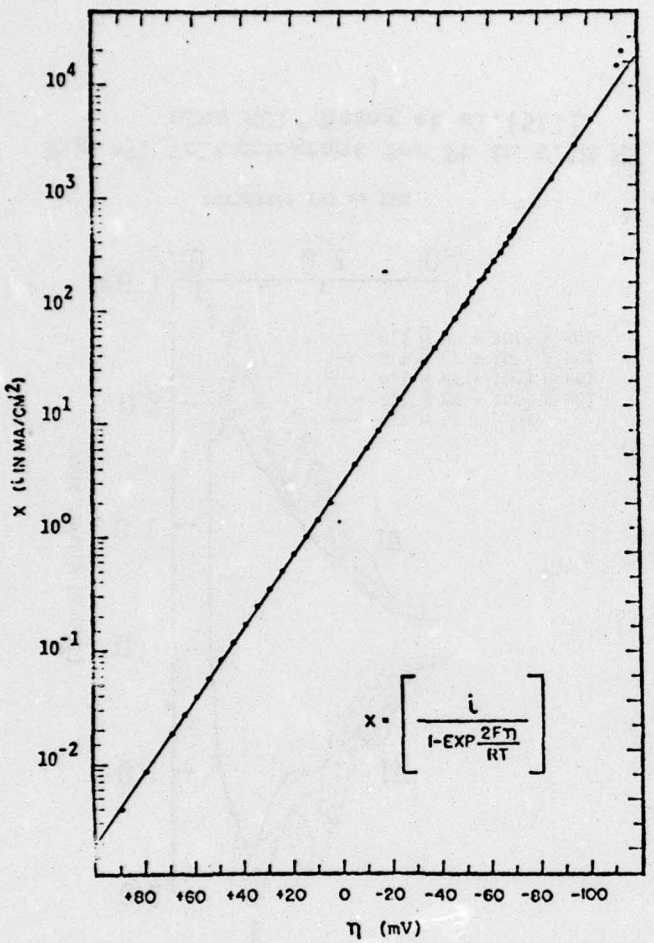

Fig. 4. Hydrogen electrode kinetics on Pt(19). Rotating Disk technique. Rotation rate: 187 Hz; T = 25 C; 6.1 M HCl. IR corrected. [see eqs. 1, 2 in text.]

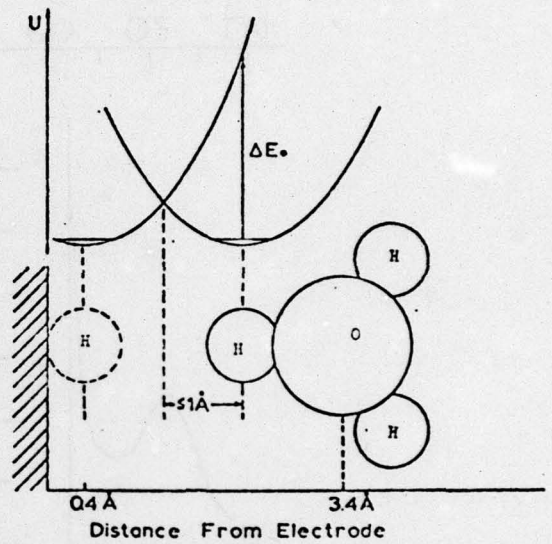

Fig. 3. Bockris-Matthews model for proton discharge (21).

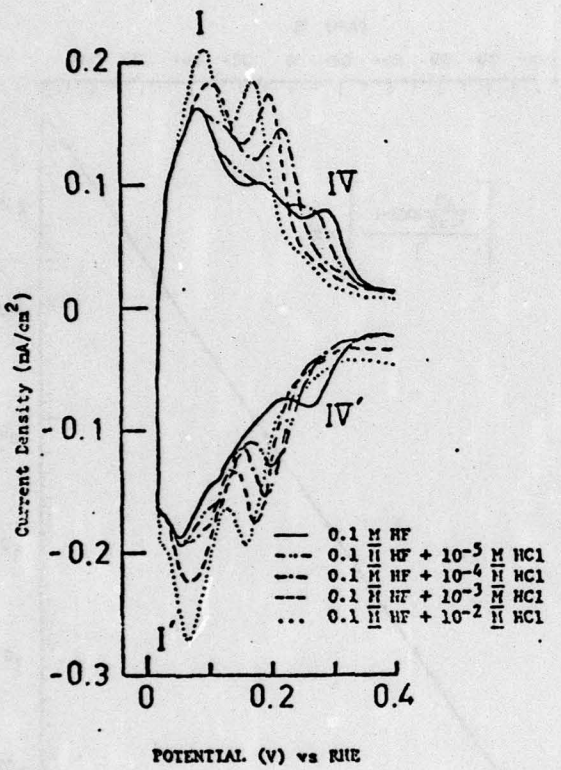

Fig. 5. Voltammograms for Pt in 0.1M HF plus HCl [Huang et al.(51)]

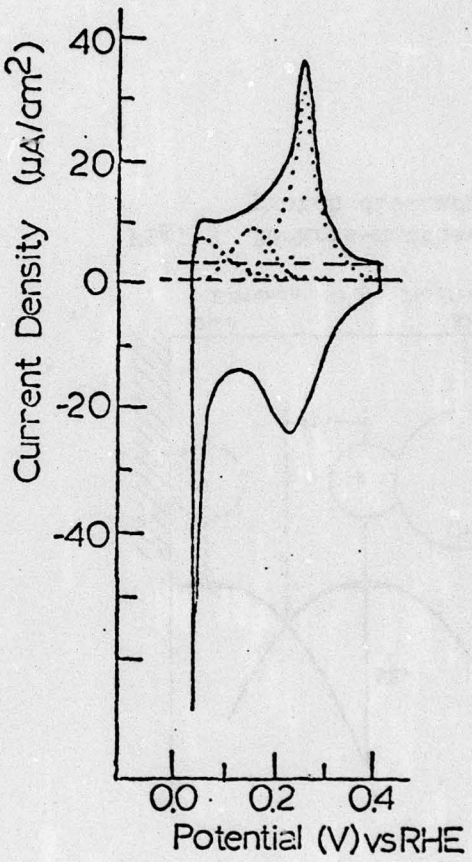

Fig. 6. Voltammogram for clean Pt(100-5x1) in 0.1N H_2SO_4. Sweep rate: 50mV/s.

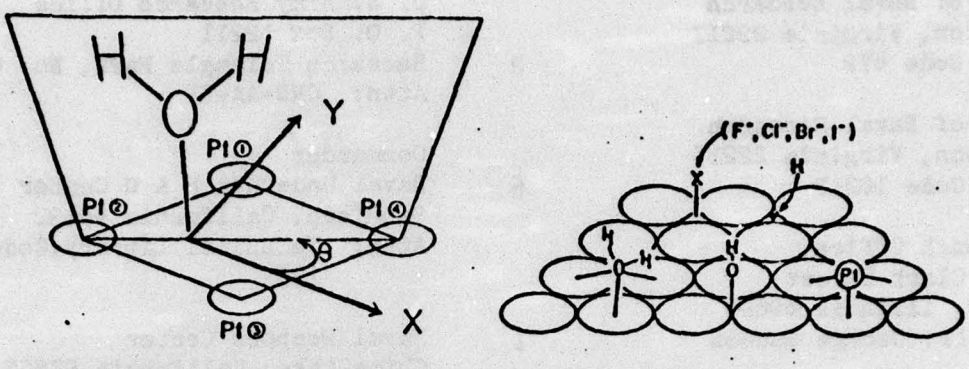

Figure 7. Adsorption sites on Pt (111) for various species. [Leban and Hubbard (65)].

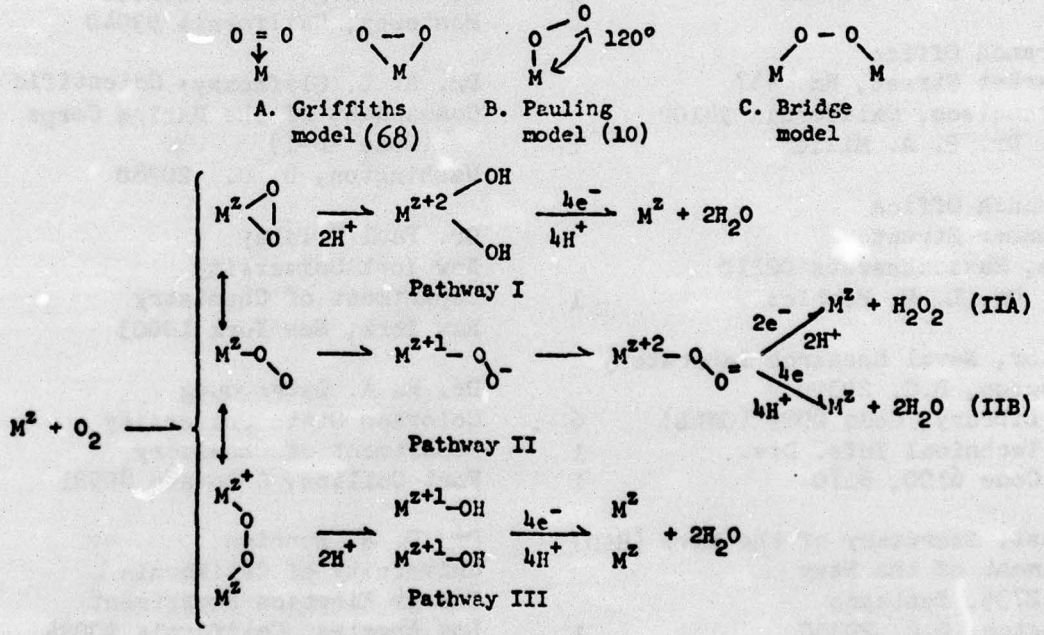

Figure 8. Reaction pathways for O_2 electroreduction. [Yeager (70)].

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